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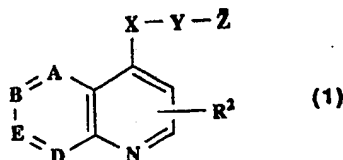
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**Windlesham Surrey, GU20 6PH(GB)**(54) **Naphthyridine derivatives.**

(57) Substituted naphthyridines of the formula (1):



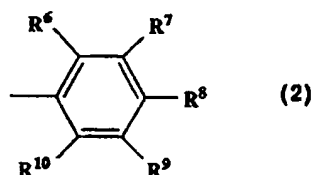
wherein

one of A, B, E, or D is N, and the others are CR<sup>1</sup>;R<sup>1</sup> and R<sup>2</sup> are independently H or halo.X is O, S, SO, SO<sub>2</sub>, NR<sup>3</sup>, or CR<sup>4</sup>R<sup>5</sup>, where R<sup>3</sup> is H, (C<sub>1</sub>-C<sub>4</sub>) alkyl, or (C<sub>1</sub>-C<sub>4</sub>) acyl, and R<sup>4</sup> and R<sup>5</sup> are independently H, (C<sub>1</sub>-C<sub>4</sub>) acyl, (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>2</sub>-C<sub>4</sub>) alkenyl or -alkynyl, CN, or OH, or R<sup>4</sup> and R<sup>5</sup> combine to form a carbocyclic ring containing four to six carbon atoms;Y is nil, Z being bonded directly to X, or Y is an alkyl chain one to six carbon atoms long, optionally including a carbocyclic ring, and optionally including a hetero atom selected from O, S, SO, SO<sub>2</sub>, NR<sup>3</sup>, or SiR<sup>19</sup>R<sup>20</sup>, where R<sup>19</sup> and R<sup>20</sup> are independently H, (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>3</sub>-C<sub>4</sub>) branched alkyl, phenyl, or substituted phenyl, and optionally substituted with (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>2</sub>-C<sub>4</sub>) alkenyl or -alkynyl, (C<sub>3</sub>-C<sub>7</sub>) branched alkyl, (C<sub>3</sub>-C<sub>7</sub>) cycloalkyl or -cycloalkenyl, halo, hydroxy, or acetyl, and

Z is

(a) a C<sub>1</sub>-C<sub>12</sub> saturated or unsaturated hydrocarbon chain, straight chain or branched optionally including a hetero atom selected from O, S, SO, SO<sub>2</sub>, NR<sup>3</sup>, or SiR<sup>19</sup>R<sup>20</sup>, and optionally substituted with halo, halo (C<sub>1</sub>-C<sub>4</sub>) alkoxy, hydroxy, (C<sub>3</sub>-C<sub>8</sub>) cycloalkyl or cycloalkenyl, or (C<sub>1</sub>-C<sub>4</sub>) acyl;(b) (C<sub>3</sub>-C<sub>8</sub>) cycloalkyl or -cycloalkenyl, optionally substituted with (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>1</sub>-C<sub>4</sub>) alkoxy, halo (C<sub>1</sub>-C<sub>4</sub>)**EP 0 410 762 A1**

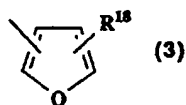
alkyl, halo (C<sub>1</sub>-C<sub>4</sub>) alkoxy, halo, hydroxy, or (C<sub>1</sub>-C<sub>4</sub>) acyl;  
 (c) a phenyl group of the formula (2)



where

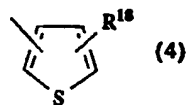
R<sup>6</sup> to R<sup>10</sup> are independently H, halo, I, (C<sub>1</sub>-C<sub>10</sub>) alkyl, (C<sub>3</sub>-C<sub>8</sub>) alkenyl or -alkynyl, branched (C<sub>3</sub>-C<sub>6</sub>) alkyl, -alkenyl, or -alkynyl, (C<sub>3</sub>-C<sub>8</sub>) cycloalkyl or -cycloalkenyl, halo (C<sub>1</sub>-C<sub>7</sub>) alkyl, (C<sub>1</sub>-C<sub>7</sub>) alkoxy, (C<sub>1</sub>-C<sub>7</sub>) alkylthio, halo (C<sub>1</sub>-C<sub>7</sub>) alkoxy, phenoxy, substituted phenoxy, phenylthio, substituted phenylthio, phenyl, substituted phenyl, NO<sub>2</sub>, acetoxy, OH, CN, SiR<sup>11</sup>R<sup>12</sup>R<sup>13</sup>, OSiR<sup>11</sup>R<sup>12</sup>R<sup>13</sup>, NR<sup>14</sup>R<sup>15</sup>, S(O)R<sup>16</sup>, or SO<sub>2</sub>R<sup>17</sup> where R<sup>11</sup>, R<sup>12</sup>, and R<sup>13</sup> are independently (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>3</sub>-C<sub>4</sub>) branched alkyl, phenyl, or substituted phenyl, R<sup>14</sup> and R<sup>15</sup> are independently H, (C<sub>1</sub>-C<sub>4</sub>) alkyl, or (C<sub>1</sub>-C<sub>4</sub>) acyl, and R<sup>16</sup> and R<sup>17</sup> are phenyl, substituted phenyl, or (C<sub>1</sub>-C<sub>4</sub>) alkyl;

(d) a furyl group of formula (3)



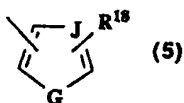
where R<sup>18</sup> is H, halo, halomethyl, CN, NO<sub>2</sub>, (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>3</sub>-C<sub>4</sub>) branched alkyl, phenyl, substituted phenyl, or (C<sub>1</sub>-C<sub>4</sub>) alkoxy;

(e) a thienyl group of the formula (4)



where R<sup>18</sup> is as defined in paragraph (d);

(f) a group of formula (5) or (6)



where R<sup>18</sup> is as defined in paragraph (d), J is N or CH, and G is O, NR<sup>21</sup>, or S, provided that if J is not N then G is NR<sup>21</sup>, where R<sup>21</sup> is H, (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>1</sub>-C<sub>4</sub>) acyl, phenylsulfonyl, or substituted phenylsulfonyl;

(g) a group selected from

optionally substituted naphthyl, dihydronaphthyl, tetrahydronaphthyl, and decahydronaphthyl;

optionally substituted pyridyl;

optionally substituted indolyl;

and 1,3-benzodioxolyl;

or an acid addition salt or N-oxide of a compound of formula (1); are plant fungicides, miticides, and insecticides.

## NAPHTHYRIDINE DERIVATIVES

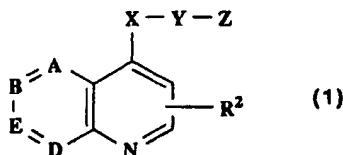
Field of the Invention

This invention provides new compounds that have excellent plant fungicide activity. Some of the compounds have also demonstrated insecticidal and miticidal activity. The invention also provides compositions and combination products that contain a compound of the invention as active ingredient, as well as providing fungicidal, miticidal, and insecticidal methods.

There is an acute need for new fungicides, insecticides, and miticides, because target pathogens are rapidly developing resistance to currently used pesticides. Widespread failure of N-substituted azole fungicides to control barley mildew was observed in 1983, and has been attributed to the development of resistance. At least 50 species of fungi have developed resistance to the benzimidazole fungicides. The field performance of DMI (demethylation inhibitor) fungicides, which are now widely relied on to protect cereal crops from powdery mildew, has declined since they were introduced in the 1970's. Even recently introduced fungicides, like the acylalanines, which initially exhibited excellent control of potato late blight and grape downy mildew in the field, have become less effective because of widespread resistance. Similarly, mites and insects are developing resistance to the miticides and insecticides in current use. Resistance to insecticides in arthropods is widespread, with at least 400 species resistant to one or more insecticides. The development of resistance to some of the older insecticides, such as DDT, the carbamates, and the organophosphates, is well known. But resistance has even developed to some of the newer pyrethroid insecticides and miticides. Therefore a need exists for new fungicides, insecticides, and miticides.

Summary of the Invention

This invention provides compounds of the formula (1):



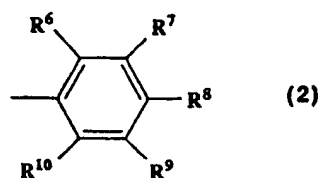
wherein

one of A, B, E, or D is N, and the others are CR<sup>1</sup>;  
R<sup>1</sup> and R<sup>2</sup> are independently H or halo.

X is O, S, SO, SO<sub>2</sub>, NR<sup>3</sup>, or CR<sup>4</sup>R<sup>5</sup>, where R<sup>3</sup> is H, (C<sub>1</sub>-C<sub>4</sub>) alkyl, or (C<sub>1</sub>-C<sub>4</sub>) acyl, and R<sup>4</sup> and R<sup>5</sup> are independently H, (C<sub>1</sub>-C<sub>4</sub>) acyl, (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>2</sub>-C<sub>4</sub>) alkenyl or -alkynyl, CN, or OH, or R<sup>4</sup> and R<sup>5</sup> combine to form a carbocyclic ring containing four to six carbon atoms;

Y is nil, Z being bonded directly to X, or Y is an alkyl chain one to six carbon atoms long, optionally including a carbocyclic ring, and optionally including a hetero atom selected from O, S, SO, SO<sub>2</sub>, NR<sup>3</sup>, or SiR<sup>19</sup>R<sup>20</sup>, where R<sup>19</sup> and R<sup>20</sup> are independently H, (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>3</sub>-C<sub>4</sub>) branched alkyl, phenyl, or substituted phenyl, and optionally substituted with (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>2</sub>-C<sub>4</sub>) alkenyl or -alkynyl, branched (C<sub>3</sub>-C<sub>7</sub>) alkyl, (C<sub>3</sub>-C<sub>7</sub>) cycloalkyl or -cycloalkenyl, halo, hydroxy, or acetyl, and  
Z is

- (a) a C<sub>1</sub>-C<sub>12</sub> saturated or unsaturated hydrocarbon chain, straight chain or branched optionally including a hetero atom selected from O, S, SO, SO<sub>2</sub>, NR<sup>3</sup>, or SiR<sup>19</sup>R<sup>20</sup>, and optionally substituted with halo, halo (C<sub>1</sub>-C<sub>4</sub>) alkoxy, hydroxy, (C<sub>3</sub>-C<sub>8</sub>) cycloalkyl or cycloalkenyl, or (C<sub>1</sub>-C<sub>4</sub>) acyl;
- (b) (C<sub>3</sub>-C<sub>8</sub>) cycloalkyl or cycloalkenyl, optionally substituted with (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>1</sub>-C<sub>4</sub>) alkoxy, halo (C<sub>1</sub>-C<sub>4</sub>) alkyl, halo (C<sub>1</sub>-C<sub>4</sub>) alkoxy, halo, hydroxy, or (C<sub>1</sub>-C<sub>4</sub>) acyl;
- (c) a phenyl group of the formula (2)

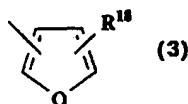


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where

- 10 R<sup>6</sup> to R<sup>10</sup> are independently H, halo, I, (C<sub>1</sub>-C<sub>10</sub>) alkyl, (C<sub>3</sub>-C<sub>8</sub>) alkenyl or -alkynyl, branched (C<sub>3</sub>-C<sub>6</sub>) alkyl, -alkenyl, or -alkynyl, (C<sub>3</sub>-C<sub>8</sub>) cycloalkyl or -cycloalkenyl, halo (C<sub>1</sub>-C<sub>7</sub>) alkyl, (C<sub>1</sub>-C<sub>7</sub>) alkoxy, (C<sub>1</sub>-C<sub>7</sub>) alkylthio, halo (C<sub>1</sub>-C<sub>7</sub>) alkoxy, phenoxy, substituted phenoxy, phenylthio, substituted phenylthio, phenyl, substituted phenyl, NO<sub>2</sub>, acetoxy, OH, CN, SiR<sup>11</sup>R<sup>12</sup>R<sup>13</sup>, OSiR<sup>11</sup>R<sup>12</sup>R<sup>13</sup>, NR<sup>14</sup>R<sup>15</sup>, S(O)R<sup>16</sup>, or SO<sub>2</sub>R<sup>17</sup> where R<sup>11</sup>, R<sup>12</sup>, and R<sup>13</sup> are independently (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>3</sub>-C<sub>4</sub>) branched alkyl, phenyl, or substituted phenyl, R<sup>14</sup> and R<sup>15</sup> are independently H, (C<sub>1</sub>-C<sub>4</sub>) alkyl, or (C<sub>1</sub>-C<sub>4</sub>) acyl, and R<sup>16</sup> and R<sup>17</sup> are phenyl, substituted phenyl, or (C<sub>1</sub>-C<sub>4</sub>) alkyl;
- 15 (d) a furyl group of formula (3)

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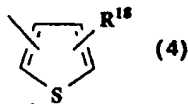


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where R<sup>18</sup> is H, halo, halomethyl, CN, NO<sub>2</sub>, (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>3</sub>-C<sub>4</sub>) branched alkyl, phenyl, substituted phenyl, or (C<sub>1</sub>-C<sub>4</sub>) alkoxy;

(e) a thienyl group of the formula (4)

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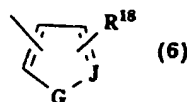
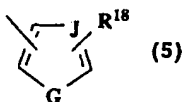


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where R<sup>18</sup> is as defined in paragraph (d);

(f) a group of formula (5) or (6)

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45 where R<sup>18</sup> is as defined in paragraph (d), J is N or CH, and G is O, NR<sup>21</sup>, or S, provided that if J is not N then G is NR<sup>21</sup>, where R<sup>21</sup> is H, (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>1</sub>-C<sub>4</sub>) acyl, phenylsulfonyl, or substituted phenylsulfonyl;

(g) a group selected from

- optionally substituted naphthyl, dihydronaphthyl, tetrahydronaphthyl, and decahydronaphthyl;
- optionally substituted pyridyl;
- optionally substituted indolyl;
- and 1,3-benzodioxolyl;

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or an acid addition salt or N-oxide of a compound of formula (1).

The fungicide combinations of the invention comprise at least 1% by weight of a compound of formula (1) in combination with a second plant fungicide.

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The fungicide compositions of the invention comprise a disease inhibiting and phytologically acceptable amount of compound of formula (1) in combination with a phytologically-acceptable carrier. Such compositions may optionally contain additional active ingredients, such as an additional fungicidal, miticidal, or insecticidal ingredient. The active ingredient typically constitutes from .001 to 99% of the composition on a weight basis.

The fungicidal method of the invention comprises applying to the locus of a plant pathogen a disease

inhibiting and phytologically acceptable amount of a compound of formula (1).

The insecticide and miticide combinations of the invention comprise at least 1% by weight of a compound of formula (1) in combination with a second insecticide or miticide.

The insecticide and miticide compositions of the invention comprise an insect- or mite-inactivating amount of a compound of formula (1) in combination with a carrier. Such compositions may optionally contain additional active ingredients, such as an additional fungicidal, miticidal, or insecticidal ingredient. The active ingredient typically constitutes from .001 to 99% of the composition on a weight basis.

The insecticidal or miticidal method of the invention comprises applying to a locus of an insect or mite an insect- or mite-inactivating amount of a compound of formula (1), or of a combination described above.

#### Detailed Description of the Invention

Throughout this document, all temperatures are given in degrees Celsius, and all percentages are weight percentages unless otherwise stated.

The term "halo" refers to a F, Cl, or Br atom.

The term "(C<sub>1</sub>-C<sub>7</sub>) alkoxy" refers to straight or branched chain alkoxy groups.

The term "(C<sub>1</sub>-C<sub>7</sub>) alkylthio" refers to straight and branched chain alkylthio groups.

The term "halo (C<sub>1</sub>-C<sub>7</sub>) alkyl" refers to a (C<sub>1</sub>-C<sub>7</sub>) alkyl group, straight chain or branched, substituted with one or more halo atoms.

The term "halo (C<sub>1</sub>-C<sub>7</sub>) alkoxy" refers to a (C<sub>1</sub>-C<sub>7</sub>) alkoxy group substituted with one or more halo groups.

The term "halo (C<sub>1</sub>-C<sub>4</sub>) alkylthio" refers to a (C<sub>1</sub>-C<sub>4</sub>) alkylthio group, straight chain or branched, substituted with one or more halo atoms.

The term "substituted phenyl" refers to phenyl substituted with up to three groups selected from halo, I, (C<sub>1</sub>-C<sub>10</sub>) alkyl, branched (C<sub>3</sub>-C<sub>6</sub>) alkyl, halo (C<sub>1</sub>-C<sub>4</sub>) alkyl, hydroxy (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>1</sub>-C<sub>4</sub>) alkoxy, halo (C<sub>1</sub>-C<sub>4</sub>) alkoxy, phenoxy, substituted phenoxy, phenyl, substituted phenyl, NO<sub>2</sub>, OH, CN, (C<sub>1</sub>-C<sub>4</sub>) alkanoyloxy, or benzyloxy.

The terms "substituted naphthyl", "substituted pyridyl" and "substituted indolyl" refer to these ring systems substituted with halo, halo (C<sub>1</sub>-C<sub>4</sub>) alkyl, CN, NO<sub>2</sub>, (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>3</sub>-C<sub>4</sub>) branched alkyl, phenyl, (C<sub>1</sub>-C<sub>4</sub>) alkoxy, or halo (C<sub>1</sub>-C<sub>4</sub>) alkoxy.

The term "substituted phenoxy" refers to phenoxy substituted with up to three groups selected from halo, I, (C<sub>1</sub>-C<sub>10</sub>) alkyl, branched (C<sub>3</sub>-C<sub>6</sub>) alkyl, halo (C<sub>1</sub>-C<sub>7</sub>) alkyl, hydroxy (C<sub>1</sub>-C<sub>7</sub>) alkyl, (C<sub>1</sub>-C<sub>7</sub>) alkoxy, halo (C<sub>1</sub>-C<sub>7</sub>) alkoxy, phenoxy, substituted phenoxy, phenyl, substituted phenyl, NO<sub>2</sub>, OH, CN, (C<sub>1</sub>-C<sub>4</sub>) alkanoyloxy, or benzyloxy.

The term "carbocyclic ring" refers to a saturated or unsaturated carbocyclic ring containing three to seven carbon atoms.

The terms "substituted phenylthio" and "substituted phenyl sulfonyl" refer to such groups substituted with up to three groups selected from halo, I, (C<sub>1</sub>-C<sub>10</sub>) alkyl, branched (C<sub>3</sub>-C<sub>6</sub>) alkyl, halo (C<sub>1</sub>-C<sub>7</sub>) alkyl, hydroxy (C<sub>1</sub>-C<sub>7</sub>) alkyl, (C<sub>1</sub>-C<sub>7</sub>) alkoxy, halo (C<sub>1</sub>-C<sub>7</sub>) alkoxy, phenoxy, substituted phenoxy, phenyl, substituted phenyl, NO<sub>2</sub>, OH, CN, (C<sub>1</sub>-C<sub>4</sub>) alkanoyloxy, or benzyloxy.

The term "unsaturated hydrocarbon chain" refers to a hydrocarbon chain containing one or two sites of unsaturation.

The term "HPLC" refers to a high-performance liquid chromatography.

#### Compounds

While all of the compounds of the invention are useful fungicides, certain classes are preferred for reasons of greater efficacy or ease of synthesis, viz:

- compounds of formula (1) wherein A is N, i.e., 1,5-naphthyridine derivatives; and
- compounds of formula (1) wherein Z is substituted phenyl.

#### Synthesis

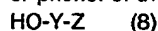
The compounds of this invention are made using well known chemical procedures. The required starting materials are commercially available, or they are readily synthesized using standard procedures.

#### 5 Synthesis of Compounds Wherein X is O

The compounds of formula (1) wherein X is O are made by condensing a compound of formula (7):



15 where  $R^2$ , A, B, E, and D are as previously defined, and L is a leaving group, such as F, Cl, Br, I,  $\text{NO}_2$ , 1,2,4-triazol-1-yl, O-SiMe<sub>3</sub>, arylthio, alkylthio, alkylsulfonyl, arylsulfonyl, alkoxy, or arylsulfinyl with an alcohol or phenol of the formula (8):



20 where

Y and Z are as previously defined.

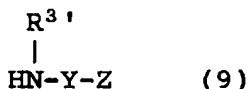
The reaction is preferably carried out in the presence of a strong base, such as sodium hydride, in a non-reactive organic solvent, such as DMF, at a temperature in the range of 0 to 25 °C.

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#### Synthesis of Compounds Wherein X is $\text{NR}^3$

The compounds of formula (1) wherein X is  $\text{NR}^3$  are prepared by condensing a compound of formula (7) with an amine of the formula (9)

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where

$\text{R}^{3'}$  is H or (C<sub>1</sub>-C<sub>4</sub>) alkyl, and

Y and Z are as previously defined.

The chloride of formula (7) is allowed to react with an appropriate amine at a wide variety of temperatures (20-180 °C), preferably in the presence of an acid acceptor, such as triethylamine. The reaction may be carried out neat, or in a non-reactive organic solvent. Compounds where  $\text{R}^3$  is acyl are prepared from amines where  $\text{R}^3$  is H, which were allowed to react with an acylating agent such as an acetyl chloride or acetic anhydride. In cases where the starting material of formula (7) is one wherein  $\text{R}^1$  or  $\text{R}^2$  is Cl, a mixture of products is obtained which are separable using liquid chromatography.

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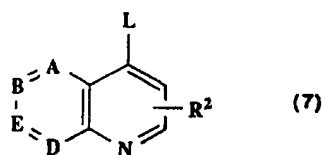
#### Synthesis of Compounds Wherein X is $\text{CR}^4\text{R}^5$

Compounds of formula (1) wherein X is  $\text{CR}^4\text{R}^5$  are prepared by reacting a compound of formula (7) where L is H with a Grignard reagent of the formula Z-Y-MgX' or a lithio reagent of the formula Z-Y-Li, where X' is halo, to provide a 3,4-dihydro naphthyridine, which is then oxidized. The desired compound of the invention may then be separated from other products using conventional means. Typical reaction conditions are those described in Armarego and Smith, J. Chem. Soc., page 5360 (1965).

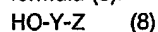
The acid addition salts and N-oxides of compounds of formula (1) are obtained in the usual way.

Accordingly, the invention also provides a process for preparing a compound of formula (1) which comprises

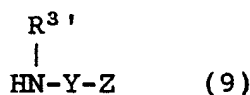
(a) condensing a compound of formula (7)



wherein  $R^1$ ,  $R^2$ , A, B, E, and D are as previously defined, and L is a leaving group, with an alcohol of the formula (8):



wherein Y and Z are as previously defined to produce a compound of formula (1) wherein X is O; or  
(b) condensing a compound of formula (7) as defined above with an amine of the formula (9)



where  $R^{3'}$  is H or  $(C_1-C_4)$  alkyl, and Y and Z are as previously defined, to provide a compound of formula (1) where X is  $\text{NR}^{3'}$ ; or

(c) acylating a compound of formula (1) wherein X is  $\text{NR}^{3'}$  to provide a compound of formula (1) wherein X is  $\text{NR}^3$  and  $R^3$  is acyl; or

(d) reacting a compound of formula (7) wherein L is H with a Grignard reagent of formula  $\text{Z-Y-MgX'}$ , where  $X'$  is halo and Z and Y are as defined above, or with a lithio reagent of formula  $\text{Z-Y-Li}$ , to provide a 3,4-dihydro naphthyridine, which is then oxidized to produce a compound of formula (1) wherein X is  $\text{CR}^4\text{R}^5$ .

#### Preparation of Naphthyridine Starting Materials

Naphthyridine starting materials are commercially available or readily prepared using conventional procedures.

For example, 1,7-naphthyridine starting materials can be prepared by the process described by R. Surrey and D. Hammer in *J. Am. Chem. Soc.* 68, 115 (1946). 1,5- and 1,6-naphthyridines can be prepared by the process described in *British Patent 1,147,760* and *Chem. Abst.* 71, 49967a (1969). 1,8-naphthyridine starting materials are prepared by the process described by W. W. Paulder and D. J. Pokorny in *J. Org. Chem.* 36, 1720 (1971) and *J. Org. Chem.* 37, 3101 (1972).

Intermediates of formula (7) wherein L is 1,2,4-triazol-1-yl, can be prepared, for example, by adding  $\text{POCl}_3$  dropwise to a mixture of a 4-hydroxynaphthyridine (1 equiv.) and 1,2,4-triazole (3 equiv.) in pyridine at room temperature.

#### Examples 1-10

The following examples are compounds actually prepared by the above described general procedures. The melting point is given for each compound. In addition, although the data has not been included, each compound was fully characterized by NMR, IR, mass spectra, and combustion analysis. Specific illustrative preparations for the compounds of Examples 4 and 7 follow the tabular listing.

EXAMPLE NUMBER	COMPOUND	M.P.
1	4-(4-fluorophenoxy)-1,8-naphthyridine	131-133 ° C
2	4-(4-fluorophenoxy)-1,7-naphthyridine	169-171 ° C
3	4-(4-fluorophenoxy)-1,6-naphthyridine	79-81 ° C
4	4-(4-fluorophenoxy)-1,5-naphthyridine	122-124 ° C
5	4-[2-[4-( t -butyl)phenyl]ethoxy]-1,5-naphthyridine	oil
6	4-[3-(4-ethoxyphenyl)propoxy]-1,5-naphthyridine	104-105 ° C
7	N-[2-[4-( t -butyl)phenyl]ethyl]-1,5-naphthyridin-4-amine	oil
8	4-(2-chlorophenoxy)-1,8-naphthyridine	126-128 ° C
9	4-[2-(4-ethoxyphenyl)ethoxy]-1,5-naphthyridine	65-66 ° C
10	N-(2-phenylethyl)-1,5-naphthyridin-4-amine	100-101 ° C

The procedures described in the following detailed examples are representative of the procedures used to prepare the compounds of the other examples.

#### Example 4

##### 4-(4-fluorophenoxy)-1,5-naphthyridine

A mixture comprising 150 mg (.911 mmole) of 4-chloro-1,5-naphthyridine and 1.00 g of 4-fluorophenol was heated at 160 ° C. After one hour, the mixture was cooled and dissolved in ethyl acetate and 2N sodium hydroxide. The organic layer was washed twice with base to remove excess 4-fluorophenol. The organic layer was then dried with magnesium sulfate and concentrated, producing an oil that slowly crystallized. This product was recrystallized in heptane, giving 103 mg of the title product. MP 122-124 ° C. Yield 47%.

#### Example 7

##### N-[2-[4-( t -butyl)phenyl]ethyl]-1,5-naphthyridin-4-amine

A mixture of 500 mg of 4-chloro-1,5-naphthyridine and 1.0 g of N-[2-[4-( t -butyl)phenyl]ethyl]amine was stirred at 130 ° C for 30 minutes. Then a 50/50 mixture of ammonium hydroxide and water was added. The product was extracted into methylene chloride, which was then concentrated. The product was purified by HPLC (silica gel, 20% ethyl acetate/80% pentane). The fractions containing the major product were collected and concentrated giving .277 mg of the title product as an oil. Yield 30%.

#### Fungicide Utility

The compounds of the present invention have been found to control fungi, particularly plant pathogens. When employed in the treatment of plant fungal diseases, the compounds are applied to the plants in a disease inhibiting and phytologically acceptable amount. The term "disease inhibiting and phytologically acceptable amount," as used herein, refers to an amount of a compound of the invention which kills or inhibits the plant disease for which control is desired, but is not significantly toxic to the plant. This amount will generally be from about 1 to 1000 ppm, with 10 to 500 ppm being preferred. The exact concentration of compound required varies with the fungal disease to be controlled, the type formulation employed, the



method of application, the particular plant species, climate conditions and the like. A suitable application rate is typically in the range from .25 to 4 lb/A. The compounds of the invention may also be used to protect stored grain and other non-plant loci from fungal infestation.

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### Greenhouse Tests

The following experiments were performed in the laboratory to determine the fungicidal efficacy of the compounds of the invention.

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### Test 1

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This screen was used to evaluate the efficacy of the present compounds against a variety of different organisms that cause plant diseases.

The test compounds were formulated for application by dissolving 50 mg of the compound into 1.25 ml of solvent. The solvent was prepared by mixing 50 ml of "Tween 20" (polyoxyethylene (20) sorbitan monoaurate emulsifier) with 475 ml of acetone and 475 ml of ethanol. The solvent/compound solution was diluted to 125 ml with deionized water. The resulting formulation contains 400 ppm test chemical. Lower concentrations were obtained by serial dilution with the solvent-surfactant mixture.

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The formulated test compounds were applied by foliar spray. The following plant pathogens and their corresponding plants were employed.

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Pathogen	Designation in Following Table	Host
<u>Erysiphe graminis tritici</u> (powdery mildew)	POWD MDEW	wheat
<u>Pyricularia oryzae</u> (rice blast)	RICE BLAS	rice
<u>Puccinia recondita tritici</u> (leaf rust)	LEAF RUST	wheat
<u>Botrytis cinerea</u> (gray mold)	GRAY MOLD	grape berries
<u>Pseudoperonospora cubensis</u> (downy mildew)	DOWN MDEW	squash
<u>Cercospora beticola</u> (leaf spot)	LEAF SPOT	sugar beet
<u>Venturia inaequalis</u> (apple scab)	APPL SCAB	apple seedling
<u>Septoria tritici</u> (leaf blotch)	LEAF BLOT	wheat

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The formulated technical compounds were sprayed on all foliar surfaces of the host plants (or cut berry) to past run-off. Single pots of each host plant were placed on raised, revolving pedestals in a fume hood. Test solutions were sprayed on all foliar surfaces. All treatments were allowed to dry and the plants were inoculated with the appropriate pathogens within 2-4 hours.

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Table 1 presents the activity of typical compounds of the present invention when evaluated in this experiment. The effectiveness of test compounds in controlling disease was rated using the following scale.

0 = not tested against specific organism

- = 0-19% control at 400 ppm

+ = 20-89% control at 400 ppm  
 ++ = 90-100% control at 400 ppm  
 +++ = 90-100% control at 100 ppm

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TABLE 1

EX. NO.	POWD MDEW	RICE BLAST	LEAF RUST	GRAY MOLD	DOWN MDEW	LEAF SPOT	APPL SCAB	LEAF BLOT
1	+	-	++	-	++	0	0	0
2	+	-	+	-	+	0	0	0
3	-	-	-	-	-	0	0	0
4	+	+	+	-	++	0	0	0
5	+	++	++	-	+++	0	0	0
6	-	-	-	-	-	0	0	0
7	++	++	+++	-	+++	0	0	0
8	-	+	+	-	++	0	0	0
9	+	++	+++	-	++	0	0	0
10	+	+	+	-	+++	+	+	-

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#### Combinations

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Fungal disease pathogens are known to develop resistance to fungicides. When strains resistant to a fungicide do develop, it becomes necessary to apply larger and larger amounts of the fungicide to obtain desired results. To retard the development of resistance to new fungicides, it is desirable to apply the new fungicides in combination with other fungicides. Use of a combination product also permits the product's spectrum of activity to be adjusted.

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Accordingly, another aspect of the invention is a fungicidal combination comprising at least 1% by weight of a compound of formula (1) in combination with a second fungicide.

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Contemplated classes of fungicides from which the second fungicide may be selected include:

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- 1) N-substituted azoles, for example propiconazole, triademefon, flusilazol, diniconazole, ethyltrianol, myclobutanil, and prochloraz;
- 2) pyrimidines, such as fenarimol and nuarimol;
- 3) morpholines, such as fenpropimorph and tridemorph;
- 4) piperazines, such as triforine; and
- 5) pyridines, such as pyrifeno.

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Fungicides in these five classes all function by inhibiting sterol biosynthesis. Additional classes of contemplated fungicides, which have other mechanisms of action include:

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- 6) dithiocarbamates, such as maneb and mancozeb;
- 7) phthalimides, such as captafol;
- 8) isophthalonitriles, such as chlorothalonil;
- 9) dicarboximides, such as iprodione;
- 10) benzimidazoles, such as benomyl and carbendazim;
- 11) 2-aminopyrimidines, such as ethirimol;
- 12) carboxamides, such as carboxin; and
- 13) dinitrophenols, such as dinocap.

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The fungicide combinations of the invention contain at least 1%, ordinarily 20 to 80%, and more typically 50 to 75% by weight of a compound of formula (1).

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#### Insecticide and Miticide Utility

The compounds of the invention are also useful for the control of insects and mites. Therefore, the

present invention also is directed to a method for inhibiting an insect or mite which comprises applying to a locus of the insect or mite an insect- or mite-inhibiting amount of a compound of formula (1).

The compounds of the invention show activity against a number of insects and mites. More specifically, the compounds show activity against melon aphid, which is a member of the insect order Homoptera. Other members of the Homoptera include leafhoppers, planthoppers, pear psylla, apple sucker, scale insects, whiteflies, spittle bugs as well as numerous other host specific aphid species. Activity has also been observed against greenhouse thrips, which are members of the order Thysanoptera. The compounds also show activity against Southern armyworm, which is a member of the insect order Lepidoptera. Other typical members of this order are codling moth, cutworm, clothes moth, Indianmeal moth, leaf rollers, corn earworm, European corn borer, cabbage worm, cabbage looper, cotton bollworm, bagworm, eastern tent caterpillar, sod webworm, and fall armyworm.

Representative mite species with which it is contemplated that the present invention can be practiced include those listed below.

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	<u>FAMILY</u>	<u>SCIENTIFIC NAME</u>	<u>COMMON NAME</u>
5	ACARIDAE	<u>Aleurobius farinae</u>	
		<u>Rhizoglyphus echinopus</u>	Bulb mite
10		<u>Rhizoglyphus elongatus</u>	
		<u>Rhizoglyphus rhizophagus</u>	
		<u>Rhizoglyphus sagittatae</u>	
		<u>Rhizoglyphus tarsalis</u>	
15			
	ERIOPHYIDAE		
		<u>Abacarus farinae</u>	Grain rust mite
20		<u>Aceria brachytarsus</u>	
		<u>Acalitus essigi</u>	Redberry mite
		<u>Aceria ficus</u>	
25		<u>Aceria fraaxinivorus</u>	
		<u>Aceria granati</u>	
		<u>Aceria parapopuli</u>	
		<u>Eriophyes sheldoni</u>	Citrus bud mite
30		<u>Aceria tulipae</u>	
		<u>Aculus carnutus</u>	Peach silver mite
		<u>Aculus schlechtendali</u>	Apple rust mite
35		<u>Colomerus vitis</u>	Grape erineum mite
		<u>Eriophyes convolvens</u>	
		<u>Eriophyes insidiosus</u>	
		<u>Eriophyes malifoliae</u>	
40		<u>Eriophyes padi</u>	
		<u>Eriophyes pruni</u>	
		<u>Epitrimerus pyri</u>	Pear leaf blister mite
45		<u>Eriophyes ramosus</u>	
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	<u>FAMILY</u>	<u>SCIENTIFIC NAME</u>	<u>COMMON NAME</u>
5		<u>Eriophyes sheldoni</u>	Citrus bud mite
		<u>Eriophyes ribis</u>	
		<u>Phyllocoptes gracilis</u>	Dryberry mite
10		<u>Phyllocoptruta oleivora</u>	Citrus rust mite
		<u>Phytoptus ribis</u>	
		<u>Trisetacus pini</u>	
		<u>Vasates amygdalina</u>	
15		<u>Vasates eurynotus</u>	
		<u>Vasates quadripedes</u>	Maple bladder gall mite
		<u>Vasates schlechtendali</u>	
20	<b>EUPODIDAE</b>		
		<u>Penthaleus major</u>	Winter grain mite
25		<u>Linopodes spp.</u>	
	<b>NALEPELLIDAE</b>		
		<u>Phyllocoptella avellanae</u>	Filbert bud mite
30	<b>PENTHALEIDAE</b>		
		<u>Halotydeus destructor</u>	
35	<b>PYEMOTIDAE</b>		
		<u>Pyemotes tritici</u>	Straw itch mite
40		<u>Siteroptes cerealium</u>	
	<b>TARSONEMIDAE</b>		
		<u>Polyphagotarsonemus latus</u>	Broad mite
45		<u>Steneotarsonemus pallidus</u>	Cyclamen mite

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	<u>FAMILY</u>	<u>SCIENTIFIC NAME</u>	<u>COMMON NAME</u>
5	TENUIPALPIDAE		
		<u>Brevipalpus californicus</u>	
		<u>Brevipalpus obovatus</u>	Privet mite
10		<u>Brevipalpus lewisi</u>	Citrus flat mite
		<u>Dolichotetranychus floridanus</u>	Pineapple flase spider mite
		<u>Tenuipalpes granati</u>	
15		<u>Tenuipalpes pacificus</u>	
	TETRANYCHIDAE		
20		<u>Bryobia arborea</u>	
		<u>Bryobia practiosa</u>	Clover mite
		<u>Bryobia rubrioculus</u>	Brown mite
25		<u>Eotetranychus coryli</u>	
		<u>Eotetranychus hicoriae</u>	Pecan deaf scorch mite
		<u>Eotetranychus lewisi</u>	
		<u>Eotetranychus sexmaculatus</u>	Sixspotted spider mite
30		<u>Eotetranychus willametti</u>	
		<u>Eotetranychus banksi</u>	Texas citrus mite
		<u>Oligonychus ilicis</u>	Southern red mite
35		<u>Oligonychus pratensis</u>	Banks grass mite
		<u>Oligonychus ununguis</u>	Spruce spider mite
		<u>Panonychus citri</u>	Citrus red mite
40		<u>Panonychus ulmi</u>	European red mite
		<u>Paratetranychus modestus</u>	
		<u>Paratetranychus pratensis</u>	
		<u>Paratetranychus viridis</u>	
45		<u>Petrobia latens</u>	Brown wheat mite

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<u>FAMILY</u>	<u>SCIENTIFIC NAME</u>	<u>COMMON NAME</u>
5	<u>Schizotetranychus celarius</u>	Bamboo spider mite
	<u>Schizotetranychus pratensis</u>	
	<u>Tetranychus canadensis</u>	Fourspotted spider mite
	<u>Tetranychus cinnabarinus</u>	Carmine spider mite
10	<u>Tetranychus mcdanieli</u>	McDaniel spider mite
	<u>Tetranychus pacificus</u>	Pacific spider mite
	<u>Tetranychus schoenei</u>	Schoene spider mite
15	<u>Tetranychus urticae</u>	Twospotted spider mite
	<u>Tetranychus turkestani</u>	Strawberry spider mite
	<u>Tetranychus desertorum</u>	Desert spider mite

20 The compounds are useful for reducing populations of insects and mites, and are used in a method of inhibiting an insect or mite population which comprises applying to a locus of the insect or arachnid an effective insect- or mite-inactivating amount of a compound of formula (1). The "locus" of insects or mites is a term used herein to refer to the environment in which the insects or mites live or where their eggs are present, including the air surrounding them, the food they eat, or objects which they contact. For example, 25 plant-ingesting insects or mites can be controlled by applying the active compound to plant parts, which the insects or mites eat, particularly the foliage. It is contemplated that the compounds might also be useful to protect textiles, paper, stored grain, or seeds by applying an active compound to such substance. The term "inhibiting an insect or mite" refers to a decrease in the numbers of living insects or mites; or a decrease in 30 the number of viable insect or mite eggs. The extent of reduction accomplished by a compound depends, of course, upon the application rate of the compound, the particular compound used, and the target insect or mite species. At least an insect-inactivating or mite-inactivating amount should be used. The terms "insect-inactivating amount" and "mite-inactivating amount" are used to describe the amount, which is sufficient to cause a measurable reduction in the treated insect or mite population. Generally an amount in 35 the range from about 1 to about 1000 ppm active compound is used.

In a preferred embodiment, the present invention is directed to a method for inhibiting a mite which comprises applying to a plant an effective mite-inactivating amount of a compound of formula (1) in accordance with the present invention.

#### 40 MITE/INSECT SCREEN

The compounds of Examples 1-10 were tested for miticidal and insecticidal activity in the following 45 mite/insect screen.

Each test compound was formulated by dissolving the compound in acetone/alcohol (50:50) mixture containing 23 g of "TOXIMUL R" (sulfonate/nonionic emulsifier blend) and 13 g of "TOXIMUL S" (sulfonate/nonionic emulsifier blend) per liter. These mixtures were then diluted with water to give the indicated concentrations.

50 Twospotted spider mites ( Tetranychus urticae Koch) and melon aphids ( Aphis gossypii Glover) were introduced on squash cotyledons and allowed to establish on both leaf surfaces. Other plants in the same treatment pot were left uninfested. The leaves were then sprayed with 5 ml of test solution using a DeVilbiss atomizing sprayer at 10 psi. Both surfaces of the leaves were covered until runoff, and then allowed to dry for one hour. Two uninfested leaves were then excised and placed into a Petri dish 55 containing larval southern armyworm ( Spodopetra eridania Cramer).

Activity on Southern corn rootworm ( Diabrotica undecimpunctata howardi Barber) was evaluated by adding two ml of tap water, a presoaked corn seed, and 15 g of dry sandy soil to a one ounce plastic container. The soil was treated with 1 mL of test solution containing a predetermined concentration of test

compound. After six to 12 hours of drying, five 2-3 instar corn rootworm larvae were added to the individual cups, which were then capped and held at 23° C.

After standard exposure periods, percent mortality and phytotoxicity were evaluated. Results for the compounds found to be active are reported in Table 3. The remaining compounds showed no activity. The

5 following abbreviations are used in Table 3:

CRW refers to corn rootworm

SAW refers to Southern armyworm

SM refers to twospotted spider mites

MA refers to melon aphids.

TABLE 3

COMPOUND	Mite/Insect Screen					
	CRW RATE	CRW RESULTS	SAW SM & MA RATE	SAW RESULTS	SM RESULTS	MA RESULTS
	PPM	%	PPM	%	%	%
1	12.00 24.00	0 0	200 400	0 0	0 0	0 0
2	12.00 24.00	0 0	200 400	0 0	40 0	30 0
3	12.00 24.00	0 0	200 400	0 0	0 0	0 0
4	24.00	0	400	0	80	80
5	12.00 24.00	0 0	200 400	0 0	100 100	50 80
6	12.00 24.00	0 0	200 400	0 0	0 0	0 0
7	12.00 24.00	0 0	200 400	0 0	90 100	90 100
8	12.00 24.00	0 0	200 400	0 0	0 0	0 0
9	12.00 24.00	0 0	200 400	0 0	40 80	100 100
10	12.00	0	200	0	0	0

#### Compositions

The compounds of this invention are applied in the form of compositions which are important  
 50 embodiments of the invention, and which comprise a compound of this invention and a phytologically-acceptable inert carrier. The compositions are either concentrated formulations which are dispersed in water for application, or are dust or granular formulations which are applied without further treatment. The compositions are prepared according to procedures and formulae which are conventional in the agricultural chemical art, but which are novel and important because of the presence therein of the compounds of this  
 55 invention. Some description of the formulation of the compositions will be given, however, to assure that agricultural chemists can readily prepare any desired composition.

The dispersions in which the compounds are applied are most often aqueous suspensions or emulsions prepared from concentrated formulations of the compounds. Such water-soluble, water-suspendable or



emulsifiable formulations are either solids usually known as wettable powders, or liquids usually known as emulsifiable concentrates or aqueous suspensions. Wettable powders, which may be compacted to form water dispersible granules, comprise an intimate mixture of the active compound, an inert carrier and surfactants. The concentration of the active compound is usually from about 10% to about 90% by weight.

5 The inert carrier is usually chosen from among the attapulgite clays, the montmorillonite clays, the diatomaceous earths, or the purified silicates. Effective surfactants, comprising from about 0.5% to about 10% of the wettable powder, are found among the sulfonated lignins, the condensed naphthalenesulfonates, the naphthalenesulfonates, the alkylbenzenesulfonates, the alkyl sulfates, and nonionic surfactants such as ethylene oxide adducts of alkyl phenols.

10 Emulsifiable concentrates of the compounds comprise a convenient concentration of a compound, such as from about 50 to about 500 grams per liter of liquid, equivalent to about 10% to about 50%, dissolved in an inert carrier which is either a water miscible solvent or a mixture of water-immiscible organic solvent and emulsifiers. Useful organic solvents include aromatics, especially the xylenes, and the petroleum fractions, especially the high-boiling naphthalenic and olefinic portions of petroleum such as heavy aromatic naphtha.

15 Other organic solvents may also be used, such as the terpenic solvents including rosin derivatives, aliphatic ketones such as cyclohexanone, and complex alcohols such as 2-ethoxyethanol. Suitable emulsifiers for emulsifiable concentrates are chosen from conventional nonionic surfactants, such as those discussed above.

Aqueous suspensions comprise suspensions of water-insoluble compounds of this invention, dispersed  
20 in an aqueous vehicle at a concentration in the range from about 5% to about 50% by weight. Suspensions are prepared by finely grinding the compound, and vigorously mixing it into a vehicle comprised of water and surfactants chosen from the same types discussed above. Inert ingredients, such as inorganic salts and synthetic or natural gums, may also be added, to increase the density and viscosity of the aqueous vehicle. It is often most effective to grind and mix the compound at the same time by preparing the aqueous  
25 mixture, and homogenizing it in an implement such as a sand mill, ball mill, or piston-type homogenizer.

The compounds may also be applied as granular compositions, which are particularly useful for applications to the soil. Granular compositions usually contain from about 0.5% to about 10% by weight of the compound, dispersed in an inert carrier which consists entirely or in large part of clay or a similar inexpensive substance. Such compositions are usually prepared by dissolving the compound in a suitable  
30 solvent, and applying it to a granular carrier which has been pre-formed to the appropriate particle size, in the range of from about 0.5 to 3 mm. Such compositions may also be formulated by making a dough or paste of the carrier and compound, and crushing and drying to obtain the desired granular particle size.

Dusts containing the compounds are prepared simply by intimately mixing the compound in powdered form with a suitable dusty agricultural carrier, such as kaolin clay, ground volcanic rock and the like. Dusts  
35 can suitably contain from about 1% to about 10% of the compound.

It is equally practical, when desirable for any reason, to apply the compound in the form of a solution in an appropriate organic solvent, usually a bland petroleum oil, such as the spray oils, which are widely used in agricultural chemistry.

Insecticides and miticides are generally applied in the form of a dispersion of the active ingredient in a  
40 liquid carrier. It is conventional to refer to application rates in terms of the concentration of active ingredient in the carrier. The most widely used carrier is water.

The compounds of the invention can also be applied in the form of an aerosol composition. In such compositions the active compound is dissolved or dispersed in an inert carrier, which is a pressure-generating propellant mixture. The aerosol composition is packaged in a container from which the mixture is  
45 dispensed through an atomizing valve. Propellant mixtures comprise either low-boiling halocarbons, which may be mixed with organic solvents, or aqueous suspensions pressurized with inert gases or gaseous hydrocarbons.

The actual amount of compound to be applied to loci of insects and mites is not critical and can readily be determined by those skilled in the art in view of the examples above. In general, concentrations of from  
50 10 ppm to 5000 ppm of compound are expected to provide good control. With many of the compounds, concentrations of from 100 to 1500 ppm will suffice. For field crops, such as soybeans and cotton, a suitable application rate for the compounds is about 0.5 to 1.5 lb/A, typically applied in 50 gal/A of spray formulation containing 1200 to 3600 ppm of compound. For citrus crops, a suitable application rate is from about 100 to 1500 gal/A spray formulation, which is a rate of 100 to 1000 ppm.

55 The locus to which a compound is applied can be any locus inhabited by an insect or arachnid, for example, vegetable crops, fruit and nut trees, grape vines, and ornamental plants. Inasmuch as many mite species are specific to a particular host, the foregoing list of mite species provides exemplification of the wide range of settings in which the present compounds can be used.

Because of the unique ability of mite eggs to resist toxicant action, repeated applications may be desirable to control newly emerged larvae, as is true of other known acaricides.

The following formulations of compounds of the invention are typical of compositions useful in the practice of the present invention.

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A. 0.75 Emulsifiable Concentrate	
N-[2-[4-( t	9.38%
-butyl)phenyl]ethyl]-1,5-naphthyridin-4-amine	
"TOXIMUL D" (nonionic/anionic surfactant blend)	2.50%
"TOXIMUL H" (nonionic/anionic surfactant blend)	2.50%
"EXXON 200" (naphthalenic solvent)	85.62%

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B. 1.5 Emulsifiable Concentrate	
4-(4-fluorophenoxy)-1,5-naphthyridine	18.50%
"TOXIMUL D"	2.50%
"TOXIMUL H"	2.50%
"EXXON 200"	76.50%

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C. 0.75 Emulsifiable Concentrate	
4-[2-[4-( t	9.38%
-butyl)phenyl]ethoxy]-1,5-naphthyridine	
"TOXIMUL D"	2.50%
"TOXIMUL H"	2.50%
"EXXON 200"	85.62%

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D. 1.0 Emulsifiable Concentrate	
4-[2-[4-( t	12.50%
-butyl)phenyl]ethoxy]-1,5-naphthyridine	
N-methylpyrrolidone	25.00%
"TOXIMUL D"	2.50%
"TOXIMUL H"	2.50%
"EXXON 200"	57.50%

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E. 1.0 Aqueous Suspension		
	4-[2-[4-( t -butyl)phenyl]ethoxy]-1,5-naphthyridine	12.00%
	"PLURONIC P-103" (block copolymer of propylene oxide and ethylene oxide, surfactant)	1.50%
5	"PROXEL GXL" (biocide/preservative)	.05%
	"AF-100" (silicon based antifoam agent)	.20%
	"REAX 88B" (lignosulfonate dispersing agent)	1.00%
	propylene glycol	10.00%
	veegum	.75%
10	xanthan	.25%
	water	74.25%

F. 1.0 Aqueous Suspension		
	N-[2-[4-( t -butyl)phenyl]ethyl]-1,5-naphthyridine-4-amine	12.50%
	"MAKON 10" (10 moles ethyleneoxide nonylphenol surfactant)	1.00%
20	"ZEOSYL 200" (silica)	1.00%
	"AF-100"	0.20%
	"AGRIWET FR" (surfactant)	3.00%
	2% xanthan hydrate	10.00%
	water	72.30%

G. 1.0 Aqueous Suspension		
	4-[2-[4-( t -butyl)phenyl]ethoxy]-1,5-naphthyridine	12.50%
30	"MAKON 10"	1.50%
	"ZEOSYL 200" (silica)	1.00%
	"AF-100"	0.20%
35	"POLYFON H" (lignosulfonate dispersing agent)	0.20%
	2% xanthan hydrate	10.00%
	water	74.60%

H. Wettable Powder		
	4-[2-[4-( t -butyl)phenyl]ethoxy]-1,5-naphthyridine	25.80%
45	"POLYFON H"	3.50%
	"SELLOGEN HR"	5.00%
	"STEPHANOL ME DRY"	1.00%
	gum arabic	0.50%
50	"HISIL 233"	2.50%
	Barden clay	61.70%

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I. Aqueous Suspension	
4-[2-[4-( t	12.40%
-butyl)phenyl]ethoxy]-1,5-naphthyridine	
"TERGITOL 158-7"	5.00%
"ZEOSYL 200"	1.00%
"AF-100"	0.20%
"POLYFON H"	0.50%
2% xanthan solution	10.00%
tap water	70.90%

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J. Emulsifiable Concentrate	
4-[2-[4-( t	12.40%
-butyl)phenyl]ethoxy]-1,5-naphthyridine	
"TOXIMUL D"	2.50%
"TOXIMUL H"	2.50%
"EXXON 200"	82.60%

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K. Wettable Powder	
4-(4-fluorophenoxy)-1,5-naphthyridine	25.80%
"SELLOGEN HR"	5.00%
"POLYFON H"	4.00%
"STEPANOL ME DRY"	2.00%
"HISIL 233"	3.00%
Barden clay	60.20%

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L. Emulsifiable Concentrate	
4-(4-fluorophenoxy)-1,5-naphthyridine	6.19%
"TOXIMUL H"	3.60%
"TOXIMUL D"	0.40%
"EXXON 200"	89.81%

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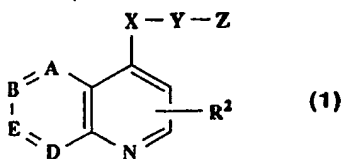
M. Wettable Powder	
4-(4-fluorophenoxy)-1,5-naphthyridine	25.80%
"SELLOGEN HR"	5.00%
"POLYFON H"	4.00%
"STEPANOL ME DRY"	2.00%
"HISIL 233"	3.00%
Barden clay	60.20%

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N. Aqueous Suspension	
N-[2-[4-(t-butyl)phenyl]ethyl]-1,5-naphthyridin-4-amine	12.40%
"TERGITOL 158-7"	5.00%
"ZEOSYL 200"	1.00%
"POLYFON H"	0.50%
"AF-100"	0.20%
xanthan solution (2%)	10.00%
tap water	70.90%

## 15 Claims

1. A naphthyridine derivative of the formula (1)



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wherein

one of A, B, E, or D is N, and the others are CR¹;

R¹ and R² are independently H or halo.

30 X is O, S, SO, SO₂, NR³, or CR⁴R⁵, where R³ is H, (C₁-C₄) alkyl, or (C₁-C₄) acyl, and R⁴ and R⁵ are independently H, (C₁-C₄) acyl, (C₁-C₄) alkyl, (C₂-C₄) alkenyl or -alkynyl, CN, or OH, or R⁴ and R⁵ combine to form a carbocyclic ring containing four to six carbon atoms;

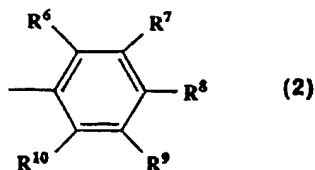
35 Y is nil, Z being directly bonded to X, or Y is an alkyl chain one to six carbon atoms long, optionally including a carbocyclic ring, and optionally including a hetero atom selected from O, S, SO, SO₂, NR³, or SiR¹⁹R²⁰, where R¹⁹ and R²⁰ are independently H, (C₁-C₄) alkyl, (C₃-C₄) branched alkyl, phenyl, or substituted phenyl, and optionally substituted with (C₁-C₄) alkyl, (C₂-C₄) alkenyl or -alkynyl, (C₃-C₇) branched alkyl, (C₃-C₇) cycloalkyl or -cycloalkenyl, halo, hydroxy, or acetyl, and

Z is

40 (a) a C₁-C₁₂ saturated or unsaturated hydrocarbon chain, straight chain or branched optionally including a hetero atom selected from O, S, SO, SO₂, or SiR¹⁹R²⁰, and optionally substituted with halo, halo (C₁-C₄) alkoxy, hydroxy, (C₃-C₈) cycloalkyl or cycloalkenyl, or (C₁-C₄) acyl;

(b) (C₃-C₈) cycloalkyl or -cycloalkenyl, optionally substituted with (C₁-C₄) alkyl, (C₁-C₄) alkoxy, halo (C₁-C₄) alkyl, halo (C₁-C₄) alkoxy, halo, hydroxy, or (C₁-C₄) acyl;

(c) a phenyl group of the formula (2)

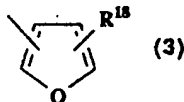


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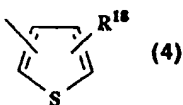
where

55 R⁶ to R¹⁰ are independently H, halo, I, (C₁-C₁₀) alkyl, (C₃-C₈) alkenyl or -alkynyl, branched (C₃-C₆) alkyl, -alkenyl, or -alkynyl, (C₃-C₈) cycloalkyl or -cycloalkenyl, halo (C₁-C₇) alkyl, (C₁-C₇) alkoxy, (C₁-C₇) alkylthio, halo (C₁-C₇) alkoxy, phenoxy, substituted phenoxy, phenylthio, substituted phenylthio, phenyl, substituted phenyl, NO₂, acetoxy, OH, CN, SiR¹¹R¹²R¹³, OSiR¹¹R¹²R¹³, NR¹⁴R¹⁵, S(O)R¹⁶, or SO₂R¹⁷

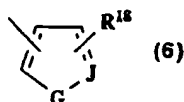
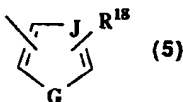
where  $R^{11}$ ,  $R^{12}$ , and  $R^{13}$  are independently (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>3</sub>-C<sub>4</sub>) branched alkyl, phenyl, or substituted phenyl,  $R^{14}$  and  $R^{15}$  are independently H, (C<sub>1</sub>-C<sub>4</sub>) alkyl, or (C<sub>1</sub>-C<sub>4</sub>) acyl, and  $R^{16}$  and  $R^{17}$  are phenyl, substituted phenyl, or (C<sub>1</sub>-C<sub>4</sub>) alkyl;  
 (d) a furyl group of formula (3)



where  $R^{18}$  is H, halo, halomethyl, CN, NO<sub>2</sub>, (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>3</sub>-C<sub>4</sub>) branched alkyl, phenyl, substituted phenyl, or (C<sub>1</sub>-C<sub>4</sub>) alkoxy;  
 (e) a thienyl group of the formula (4)

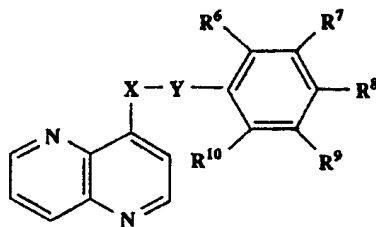


where  $R^{18}$  is as defined in paragraph (d);  
 (f) a group of formula (5) or (6)



where  $R^{18}$  is as defined in paragraph (d), J is N or CH, and G is O, NR<sup>21</sup>, or S, provided that if J is not N then G is NR<sup>21</sup>, where  $R^{21}$  is H, (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>1</sub>-C<sub>4</sub>) acyl, phenylsulfonyl, or substituted phenylsulfonyl;  
 (g) a group selected from  
 optionally substituted naphthyl, dihydronaphthyl, tetrahydronaphthyl, and decahydronaphthyl;  
 optionally substituted pyridyl;  
 optionally substituted indolyl;  
 and 1,3-benzodioxolyl;  
 or an acid addition salt or N-oxide of a compound of formula (1).

2. A compound of claim 1 wherein X is O.
3. A compound of claim 1 wherein X is NH.
4. A compound of the formula



wherein

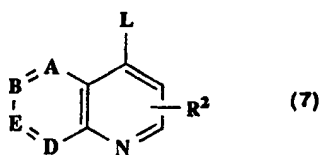
X is O or NH;

Y is nil, CH<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, or C<sub>3</sub>H<sub>6</sub>; and

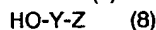
$R^6$  to  $R^{10}$  are independently H, halo, I, (C<sub>1</sub>-C<sub>10</sub>) alkyl, (C<sub>3</sub>-C<sub>8</sub>) alkenyl or -alkynyl, branched (C<sub>3</sub>-C<sub>6</sub>) alkyl, -alkenyl, or -alkynyl, (C<sub>3</sub>-C<sub>8</sub>) cycloalkyl or -cycloalkenyl, halo (C<sub>1</sub>-C<sub>7</sub>) alkyl, (C<sub>1</sub>-C<sub>7</sub>) alkoxy, (C<sub>1</sub>-C<sub>7</sub>) alkylthio, halo (C<sub>1</sub>-C<sub>7</sub>) alkoxy, phenoxy, substituted phenoxy, phenylthio, substituted phenylthio, phenyl, substituted

phenyl, NO<sub>2</sub>, acetoxy, OH, CN, SiR<sup>11</sup>R<sup>12</sup>R<sup>13</sup>, OSiR<sup>11</sup>R<sup>12</sup>R<sup>13</sup>, NR<sup>14</sup>R<sup>15</sup>, S(O)R<sup>16</sup>, or SO<sub>2</sub>R<sup>17</sup> where R<sup>11</sup>, R<sup>12</sup>, and R<sup>13</sup> are independently (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>3</sub>-C<sub>4</sub>) branched alkyl, phenyl, or substituted phenyl, R<sup>14</sup> and R<sup>15</sup> are independently H, (C<sub>1</sub>-C<sub>4</sub>) alkyl, or (C<sub>1</sub>-C<sub>4</sub>) acyl, and R<sup>16</sup> and R<sup>17</sup> are phenyl, substituted phenyl, or (C<sub>1</sub>-C<sub>4</sub>) alkyl.

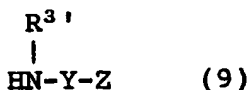
- 5 5. A fungicidal method which comprises applying to the locus of a plant pathogen a disease inhibiting and phytologically acceptable amount of a compound of formula (1).
6. A fungicide composition which comprises a compound of formula (1) in combination with a phytologically-acceptable carrier.
7. An insecticidal or miticidal method which comprises applying to the locus of an insect or mite an insect- or mite-inactivating amount of a compound of formula (1).
- 10 8. An insecticide or miticide composition which comprises a compound of formula (1) in combination with a carrier.
9. A process for preparing a compound of formula (1) as defined in claim 1 which comprises
  - (a) condensing a compound of formula (7)



wherein R<sup>1</sup>, R<sup>2</sup>, A, B, E, and D are as previously defined, and L is a leaving group, with an alcohol of the formula (8):



wherein Y and Z are as previously defined to produce a compound of formula (1) wherein X is O; or  
(b) condensing a compound of formula (7) as defined above with an amine of the formula (9)



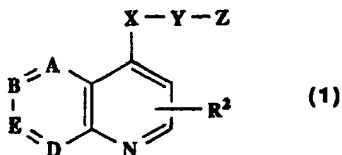
where R<sup>3</sup> is H or (C<sub>1</sub>-C<sub>4</sub>) alkyl, and Y and Z are as previously defined, to provide a compound of formula (1) where X is NR<sup>3</sup>; or

(c) acylating a compound of formula (1) wherein X is NR<sup>3</sup> to provide a compound of formula (1) wherein X is NR<sup>3</sup> and R<sup>3</sup> is acyl; or

(d) reacting a compound of formula (7) wherein L is H with a Grignard reagent of formula Z-Y-MgX', where X' is halo and Z and Y are as defined above, or with a lithio reagent of formula Z-Y-Li, to provide a 3,4-dihydro naphthyridine, which is then oxidized to produce a compound of formula (1) wherein X is CR<sup>4</sup>R<sup>5</sup>.

Claims for the following Contracting State: ES

1. An agrichemical formulation comprising a phytologically acceptable carrier in combination with from .001 to 99% by weight of a naphthyridine derivative of the formula (1)



wherein

one of A, B, E, or D is N, and the others are CR<sup>1</sup>;

R<sup>1</sup> and R<sup>2</sup> are independently H or halo.

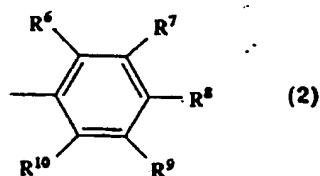
X is O, S, SO, SO<sub>2</sub>, NR<sup>3</sup>, or CR<sup>4</sup>R<sup>5</sup>, where R<sup>3</sup> is H, (C<sub>1</sub>-C<sub>4</sub>) alkyl, or (C<sub>1</sub>-C<sub>4</sub>) acyl, and R<sup>4</sup> and R<sup>5</sup> are independently H, (C<sub>1</sub>-C<sub>4</sub>) acyl, (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>2</sub>-C<sub>4</sub>) alkenyl or -alkynyl, CN, or OH, or R<sup>4</sup> and R<sup>5</sup> combine

to form a carbocyclic ring containing four to six carbon atoms;

Y is nil, Z being directly bonded to X, or Y is an alkyl chain one to six carbon atoms long, optionally including a carbocyclic ring, and optionally including a hetero atom selected from O, S, SO, SO<sub>2</sub>, NR<sup>3</sup>, or SiR<sup>19</sup>R<sup>20</sup>, where R<sup>19</sup> and R<sup>20</sup> are independently H, (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>3</sub>-C<sub>4</sub>) branched alkyl, phenyl, or substituted phenyl, and optionally substituted with (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>2</sub>-C<sub>4</sub>) alkenyl or -alkynyl, (C<sub>3</sub>-C<sub>7</sub>) branched alkyl, (C<sub>3</sub>-C<sub>7</sub>) cycloalkyl or -cycloalkenyl, halo, hydroxy, or acetyl, and

Z is

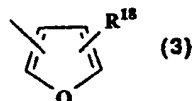
- (a) a C<sub>1</sub>-C<sub>12</sub> saturated or unsaturated hydrocarbon chain, straight chain or branched optionally including a hetero atom selected from O, S, SO, SO<sub>2</sub>, or SiR<sup>19</sup>R<sup>20</sup>, and optionally substituted with halo, halo (C<sub>1</sub>-C<sub>4</sub>) alkoxy, hydroxy, (C<sub>3</sub>-C<sub>8</sub>) cycloalkyl or cycloalkenyl, or (C<sub>1</sub>-C<sub>4</sub>) acyl;
- (b) (C<sub>3</sub>-C<sub>8</sub>) cycloalkyl or -cycloalkenyl, optionally substituted with (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>1</sub>-C<sub>4</sub>) alkoxy, halo (C<sub>1</sub>-C<sub>4</sub>) alkyl, halo (C<sub>1</sub>-C<sub>4</sub>) alkoxy, halo, hydroxy, or (C<sub>1</sub>-C<sub>4</sub>) acyl;
- (c) a phenyl group of the formula (2)



where

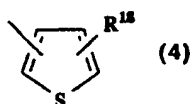
R<sup>6</sup> to R<sup>10</sup> are independently H, halo, I, (C<sub>1</sub>-C<sub>10</sub>) alkyl, (C<sub>3</sub>-C<sub>8</sub>) alkenyl or -alkynyl, branched (C<sub>3</sub>-C<sub>6</sub>) alkyl, -alkenyl, or -alkynyl, (C<sub>3</sub>-C<sub>8</sub>) cycloalkyl or -cycloalkenyl, halo (C<sub>1</sub>-C<sub>7</sub>) alkyl, (C<sub>1</sub>-C<sub>7</sub>) alkoxy, (C<sub>1</sub>-C<sub>7</sub>) alkylthio, halo (C<sub>1</sub>-C<sub>7</sub>) alkoxy, phenoxy, substituted phenoxy, phenylthio, substituted phenylthio, phenyl, substituted phenyl, NO<sub>2</sub>, acetoxy, OH, CN, SiR<sup>11</sup>R<sup>12</sup>R<sup>13</sup>, OSiR<sup>11</sup>R<sup>12</sup>R<sup>13</sup>, NR<sup>14</sup>R<sup>15</sup>, S(O)R<sup>16</sup>, or SO<sub>2</sub>R<sup>17</sup> where R<sup>11</sup>, R<sup>12</sup>, and R<sup>13</sup> are independently (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>3</sub>-C<sub>4</sub>) branched alkyl, phenyl, or substituted phenyl, R<sup>14</sup> and R<sup>15</sup> are independently H, (C<sub>1</sub>-C<sub>4</sub>) alkyl, or (C<sub>1</sub>-C<sub>4</sub>) acyl, and R<sup>16</sup> and R<sup>17</sup> are phenyl, substituted phenyl, or (C<sub>1</sub>-C<sub>4</sub>) alkyl;

(d) a furyl group of formula (3)



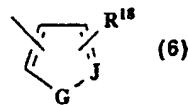
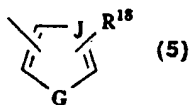
where R<sup>18</sup> is H, halo, halomethyl, CN, NO<sub>2</sub>, (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>3</sub>-C<sub>4</sub>) branched alkyl, phenyl, substituted phenyl, or (C<sub>1</sub>-C<sub>4</sub>) alkoxy;

(e) a thienyl group of the formula (4)



where R<sup>18</sup> is as defined in paragraph (d);

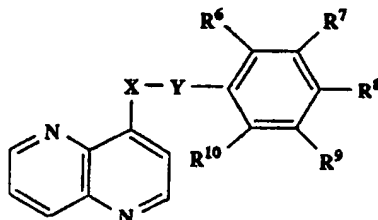
(f) a group of formula (5) or (6)



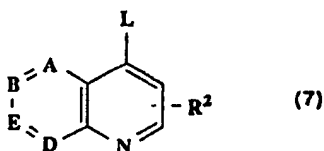
where R<sup>18</sup> is as defined in paragraph (d), J is N or CH, and G is O, NR<sup>21</sup>, or S, provided that if J is not N then G is NR<sup>21</sup>, where R<sup>21</sup> is H, (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>1</sub>-C<sub>4</sub>) acyl, phenylsulfonyl, or substituted phenylsulfonyl;



- (g) a group selected from  
 optionally substituted naphthyl, dihydronaphthyl, tetrahydronaphthyl, and  
 decahydronaphthyl;  
 optionally substituted pyridyl;  
 optionally substituted indolyl;  
 and 1,3-benzodioxolyl;  
 or an acid addition salt or N-oxide of a compound of formula (1).
2. A composition of claim 1 wherein the compound of formula (1) is one in which X is O.
3. A composition of claim 1 wherein the compound of formula (1) is one in which X is NH.
4. An agricultural composition of claim 1 wherein the active ingredient is a compound of the formula



- wherein  
 X is O or NH;  
 Y is nil, CH<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, or C<sub>3</sub>H<sub>6</sub>; and  
 R<sup>6</sup> to R<sup>10</sup> are independently H, halo, I, (C<sub>1</sub>-C<sub>10</sub>) alkyl, (C<sub>3</sub>-C<sub>8</sub>) alkenyl or -alkynyl, branched (C<sub>3</sub>-C<sub>6</sub>) alkyl,  
 -alkenyl, or -alkynyl, (C<sub>3</sub>-C<sub>8</sub>) cycloalkyl or -cycloalkenyl, halo (C<sub>1</sub>-C<sub>7</sub>) alkyl, (C<sub>1</sub>-C<sub>7</sub>) alkoxy, (C<sub>1</sub>-C<sub>7</sub>) alkylthio,  
 halo (C<sub>1</sub>-C<sub>7</sub>) alkoxy, phenoxy, substituted phenoxy, phenylthio, substituted phenylthio, phenyl, substituted  
 phenyl, NO<sub>2</sub>, acetoxy, OH, CN, SiR<sup>11</sup>R<sup>12</sup>R<sup>13</sup>, OSiR<sup>11</sup>R<sup>12</sup>R<sup>13</sup>, NR<sup>14</sup>R<sup>15</sup>, S(O)R<sup>16</sup>, or SO<sub>2</sub>R<sup>17</sup> where R<sup>11</sup>, R<sup>12</sup>,  
 and R<sup>13</sup> are independently (C<sub>1</sub>-C<sub>4</sub>) alkyl, (C<sub>3</sub>-C<sub>4</sub>) branched alkyl, phenyl, or substituted phenyl, R<sup>14</sup> and R<sup>15</sup>  
 are independently H, (C<sub>1</sub>-C<sub>4</sub>) alkyl, or (C<sub>1</sub>-C<sub>4</sub>) acyl, and R<sup>16</sup> and R<sup>17</sup> are phenyl, substituted phenyl, or (C<sub>1</sub>-  
 C<sub>4</sub>) alkyl.
5. A fungicidal method which comprises applying to the locus of a plant pathogen a disease inhibiting and  
 phytologically acceptable amount of a composition of claim 1.
6. An insecticidal or miticidal method which comprises applying to the locus of an insect or mite an insect-  
 or mite-inactivating amount of a composition of claim 1.
7. A process for preparing a compound of formula (1) as defined in claim 1 which comprises  
 (a) condensing a compound of formula (7)



- wherein R<sup>1</sup>, R<sup>2</sup>, A, B, E, and D are as previously defined, and L is a leaving group, with an alcohol of the  
 formula (8):  
 HO-Y-Z (8)  
 wherein Y and Z are as previously defined to produce a compound of formula (1) wherein X is O; or  
 (b) condensing a compound of formula (7) as defined above with an amine of the formula (9)



where R<sup>3'</sup> is H or (C<sub>1</sub>-C<sub>4</sub>) alkyl, and Y and Z are as previously defined, to provide a compound of  
 formula (1) where X is NR<sup>3'</sup>; or

(c) acylating a compound of formula (1) wherein X is  $\text{NR}^3$  to provide a compound of formula (1) wherein X is  $\text{NR}^3$  and  $\text{R}^3$  is acyl; or

(d) reacting a compound of formula (7) wherein L is H with a Grignard reagent of formula  $\text{Z-Y-MgX}'$ , where  $\text{X}'$  is halo and Z and Y are as defined above, or with a lithio reagent of formula  $\text{Z-Y-Li}$ , to provide a 3,4-dihydro naphthyridine, which is then oxidized to produce a compound of formula (1) wherein X is  $\text{CR}^4\text{R}^5$ .

8. A process for preparing the agricultural formulation of claim 1 which comprises admixing the compound of formula 1 with the carrier.

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European Patent  
Office

# EUROPEAN SEARCH REPORT

Application number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 90308216.2
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.)
A	<u>EP - A1 - 0 275 520</u> (BASF) * Abstract, claims 1,2,6,7 * ---	1-9	C 07 D 471704 A 01 N 43/90 //(C 07 D 471/04 C 07 D 221:00 C 07 D 221:00)
A	<u>GB - A - 1 566 693</u> (MERCK) * Page 1, formulas I-VI * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.)
			C 07 D 471/00 A 01 N 43/00
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 27-09-1990	Examiner ONDER
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	